An improved upper bound for the free energy of a single chain lattice model

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All the other splittings are less than 1 μeV, which are not detectable.

Heat capacity anomalies calculated for pure species are shown in Fig. 1 for 0.1 K $< T <$ 7 K. As expected from the level schemes, the peak heights for the three species are in the order of $NHD_3^+ > NH_2D_2^+ > NH_3D^+$. It should be noted that if the rotation around one of the threefold axes is much easier to occur than those around the other axes, this order of peak heights will be reversed, because in that case the signs of $\delta(T_x)$, $\delta(T_y)$, and $\delta(T_z)$ are all negative. Thus, a heat capacity measurement will clarify the situation. In the actual experiment, deuteron substitution is thought to occur randomly. In that case, the contribution of each species can be obtained from data with at least three different deuteron concentrations.

Note added in proof. Hüller [Phys. Rev. B **16**, 1844 (1977)] shows that Choi *et al.* data are compatible with the neutron scattering spectra. In the context of Ref. 6, this means that the E_1 component of the librational force constant is significant in magnitude. Since this component is related to $\epsilon(E_1)$ which affects the $NH_2D_2^+$ levels, the hear capacity for $NH_2D_2^+$ may well be different from that of Fig. 1.

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In recent publications, Gujrati *et al.*[1,2] considered a system consisting of a single chain on a square lattice. They studied the limiting case in which the chain is required to cover the whole lattice and to visit each lattice site only once, a problem equivalent to the Hamiltonian walk problem.[3,4] In analogy with real polymers, different weights are assigned to *gauche* and *trans* bonds, where the term *gauche* refers to two sequential steps at right angles and the term *trans* to two sequential steps in the same direction. Gujrati and Goldstein showed that, in contrast to the predictions of the Flory/Huggins approximation,[5] the model is never completely ordered for any positive temperature T. Their proof is based on the explicit construction of a subset of possible conformations resulting in an upper bound $\bar{f}_H(T)$ for the real free energy $f_H(T)$. For low temperatures their best upper bound is given by[2]

$$\bar{f}_H(T) \simeq \frac{-kT}{3.61} \exp(-4\epsilon/kT) , \qquad (1)$$

where ϵ is the energy difference between a *gauche* and a *trans* bond and k the Boltzmann's constant. We will in a very simple way derive a lower upper bound from

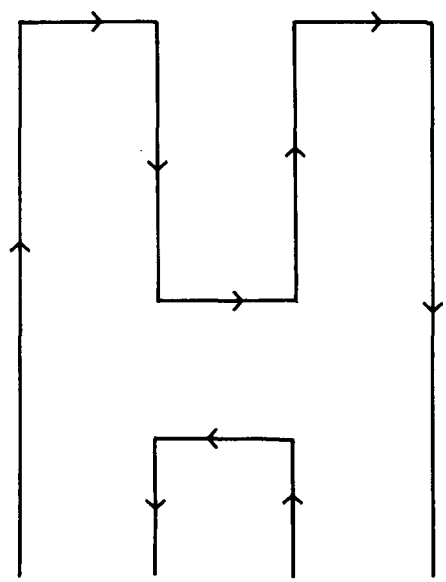

FIG. 1. Part of a Hamiltonian walk with Manhattan traffic rule showing that at most two *gauche* bonds correspond to a horizontal (or vertical) bond.

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Kasteleyn's[3,4] analytic solution for Hamiltonian walks on a square lattice oriented according to the Manhattan traffic rule. Briefly, this rule states that the orientations along the successive rows and columns alternate like the alternating one-way streets in force in Manhattan.

The exact solution of Kasteleyn for the free energy per lattice site of a single chain on a square lattice with the Manhattan constraint is given by

$$f_{MH}(T)=\frac{-kT}{(2\pi)^2}\int_0^{\pi} dw_1 \int_0^{\pi} dw_2 \ln 4(z_1^4 \sin^2 w_1 + z_2^4 \sin^2 w_2)\,, \tag{2}$$

where z_1 and z_2 are the weights of the horizontal and vertical bonds, respectively. This model deviates from the one studied by Gujrati and Goldstein not only by the Manhattan constraint but also by the way in which weights are assigned to the various bonds. It nevertheless leads to an upper bound for the free energy of the model of interest. To see this we note that every horizontal (or vertical) bond corresponds to at most two *gauche* bonds (see Fig. 1). Equation (2) therefore gives an upperbound $\tilde{f}_{MH}(T)$ for $f_H(T)$ if we take $z_1=\exp(-2\epsilon/kT)$ and $z_2=1$:

$$\begin{aligned}\tilde{f}_{MH}(T) &= \frac{-kT}{(2\pi)^2}\int_0^{\pi} dw_1 \int_0^{\pi} dw_2 \ln 4[\exp(-8\epsilon/kT)\sin^2 w_1 + \sin^2 w_2] \\ &= \frac{-4kT}{(2\pi)^2}\int_0^1 \frac{dx}{\sqrt{1-x^2}} \int_0^1 \frac{dy}{\sqrt{1-y^2}} \ln 4[\exp(-8\epsilon/kT)x^2 + y^2] \\ &= \frac{-kT}{\pi}\int_0^1 \frac{dx}{\sqrt{1-x^2}} \ln[\exp(-4\epsilon/kT)x \\ &\quad + \sqrt{\exp(-8\epsilon/kT)x^2+1}]\,. \end{aligned} \tag{3}$$

From this expression it follows simply that the low temperature approximation for the upper bound is given by

$$\tilde{f}_{MH}(T)\simeq\frac{-kT}{\pi}\exp(-4\epsilon/kT)\,. \tag{4}$$

This result is slightly better but very similar to the result of Gujrati and Goldstein mentioned before.

To understand this similarity we note first that Gordon *et al.*[6] have argued that the Manhattan traffic regulation is not an essential constraint. According to their results it is not unlikely that the number of Hamiltonian walks of length N on a square lattice with or without the Manhattan constraint is asymptotically equal to 1.338^N for large N. Moreover, all the conformations taken into account by Gujrati and Goldstein[2] that satisfy the Manhattan constraint are also counted with the correct Boltzmann factor in the construction of our upper bound.

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On representation of electron–electron repulsion energies by simple one-electron functionals

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The treatment of electron–electron repulsion energies is the bottleneck of quantum chemical calculations on atomic and molecular systems. In recent publications, bounds to the Coulomb[1,2] and exchange[3] components of the electron repulsion energy have been obtained in terms of simple one-electron functionals. Parr, Gadre, and Bartolotti[4] developed a local density functional model in which the total electron–electron repulsion energy was represented as $V_{ee}=0.754\,N^{2/3}\int\rho^{4/3}d\tau$, where N is the number of the electrons in the system and $\rho(r)$, the electron density. This model yields reasonable values of total energies, and components thereof, and also fair estimates of $\langle r^n\rangle$ expectation values. Gadre and Pathak[5] used the bound in Ref. 2 to carry out calculations of the helium atom and the hydrogen molecule using simple wave functions. Typical errors in their energies, from the corresponding variational ones obtained by an accurate representation of V_{ee}, were 2%. The equilibrium distance in the case of H_2 turned out to be quite accurate (error ~ 1%). The force constant was also predicted correctly to within 2%. With this encouraging experience, the representation of the Coulomb energies (J) and the electron–electron repulsion energies (V_{ee}) seemed to us a worthwhile project to embark upon. Here, we present the results of our analysis of the various func-

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